

HIGHLY OVER-BASED LIGHT COLORED LIQUID
ALKALINE EARTH METAL CARBOXYLATE

5 While the remainder of the description of the present invention will focus upon barium as the alkaline earth metal species, the present technology is useful with other alkaline earth metal-containing stabilizers, including those comprising calcium and strontium.

10 The use of over-based barium in formulating products for the stabilization of halogen-containing polymers is well known and is described, for example, in U.S. Pat. Nos. 3,194,823, 4,159,973, and 4,252,698. Alkyl phenols have been commonly used to promote the over-basing chemistry of
15 alkaline-earth metals. The use of an alkyl phenol also contributes a darker color for the final product. Even though these dark colored over-based barium products are suitable for the stabilization of halogen-containing polymers, their darker color results in the discoloration
20 of the finished goods and is described, for example, in U.S. Pat. Nos. 5,830,935 and 5,859,267.

U.S Patent Nos. 4,665,117, 5,830,935 and 5,859,267 describe the formation of light colored alkaline-earth metal salts where the alkyl phenol is converted to a non-
25 colored species. The products obtained as per these patents may contain residual amounts of alkyl phenol and hence are not deemed suitable for applications where substantially (alkyl) phenol-free chemistry is desired.

European Patent Publication No. 279,493 describes the
30 preparation of basic alkaline-earth metal salts of organic carboxylic acids by utilizing a mixture of aromatic and aliphatic carboxylic acids. The salts obtained in this way have dispersant properties suitable for use in lubricating

oil and fuel compositions. This patent doesn't describe the use of such compositions in stabilizing halogen-containing polymer compositions.

U.S. Published Patent Application. No. 2003/0119683
5 describes the preparation of over-based barium complexes wherein one of the reagents is an alkaline earth carboxylate of a fatty acid containing from 12 to 22 carbon atoms in the fatty alkyl group.

The present invention is a process for preparing a
10 highly over-based, (alkyl) phenol-free, light colored alkaline-earth metal organic complex of a carboxylic acid and its use in formulating stabilizer compositions for halogen-containing polymers.

In accordance with the present invention, the acid
15 reagent that is used is a non-fatty alkyl-containing acid, such as one containing an aliphatic moiety less than or equal to C₈, an aromatic group-containing acid, or mixtures thereof. For example, the process involves reacting a basic alkaline-earth metal compound, such as barium, a
20 glycol or glycol ether (which brings the barium reagent into solution), a carboxylic acid of the type just described, and carbon dioxide in a hydrocarbon solvent to produce a light colored over-based metal organic salt. A fatty alcohol, a glycol or glycol derivative is used as a
25 solubilizing agent to keep the final product well dispersed in the reaction medium.

The alkaline earth metal compound that is employed can be present in the form of a hydroxide or oxide.

The alcohol and/or glycol that can be employed can be
30 selected from those conventionally used in preparing overbased alkaline earth metal compositions of the general type represented by the instant invention. The alkyl

moiety can contain up to about 20 carbon atoms therein. Representative alcohols include oleyl alcohol and cetyl alcohol. Glycol-containing reagents include dipropylene glycol methyl ether, dipropylene glycol butyl ether, propylene glycol ethyl ether, propylene glycol butyl ether, tripropylene glycol, triethylene glycol, the glycol ester of a fatty acid, and the like. These reagents should not be in amount less than about 0.1%, and they are more preferably used at a level of from about 3% to about 5%, based on the weight of total reagent content.

The carboxylic acid may either contain an alkyl group of up to eight carbon atoms or either an alkyl-substituted or unsubstituted aromatic group, and is of the formula $R''\text{COOH}$, where R'' is the alkyl group of the foregoing type or alkyl-substituted or unsubstituted aromatic group. A representative acid for use is 2-ethylhexanoic acid. The molar ratio of barium compound to such acid in the initial reaction medium is from about 2.5 to about 7.5 moles for each mole of acid.

The solvent is chosen to achieve low odor and low volatility and can be a hydrocarbon, mineral oil, or hydrocarbon/mineral oil mixtures of low aromatic content.

The metal content of the product can be as high as 40% when made by this process route. The final product is highly over-based and (alkyl) phenol-free and possesses a very light color and can be used to make very light colored heat stabilizers.

Heat stabilizer formulations can be easily made using this new highly over-based, (alkyl) phenol-free barium and its performance, when compared against alkyl phenol-derived over-based barium, exhibited slightly better initial to mid-term color hold.

The following Examples illustrate certain embodiments of the present invention:

Example 1

A one-liter resin kettle, equipped with a mechanical stirrer, distillation condenser and a thermometer, was charged with 173 g of mineral spirits, 83 g of 2-ethyl hexanoic acid, 34 g of oleyl alcohol, 21 g of methyl carbitol and 331 g of barium hydroxide monohydrate. The reactor contents were then heated slowly to 140°C, and water was removed. Carbon dioxide was then turned on at a rate of 1 LPM (liter per minute) for 1 to 1.5 hours, and water of the reaction was removed. Mineral spirits was then replaced with a mineral oil. The product was filtered using a filter aid at 140°C and a very light colored liquid product containing 40% barium was obtained.

Example 2

A one-liter resin kettle, equipped with a mechanical stirrer, distillation condenser and a thermometer, was charged with 124 g of mineral spirits, 83 g of 2-ethyl hexanoic acid, 34 g of oleyl alcohol, 70 g of tripropylene glycol and 331 g of barium hydroxide monohydrate. The reactor contents were then heated slowly to 140°C, and water was removed. Carbon dioxide was then turned on at a rate of 1 LPM (liter per minute) for 1 to 1.5 hours, and water of the reaction was removed. The product was filtered using a filter aid at 140°C and a very light colored liquid product containing 33% barium was obtained.

Example 3

A one-liter resin kettle, equipped with a mechanical stirrer, distillation condenser and a thermometer, was

charged with 124 g of mineral spirits, 83 g of 2-ethyl hexanoic acid, 34 g of oleyl alcohol, 70 g of butyl carbitol and 331 g of barium hydroxide monohydrate. The reactor contents were then heated slowly to 140°C, and water was removed. Carbon dioxide was then turned on at a rate of 1 LPM (liter per minute) for 1 to 1.5 hours, and water of the reaction was removed. The product was filtered using a filter aid at 140°C and a very light colored liquid product containing 32% barium was obtained.

Example 4

A one-liter resin kettle, equipped with a mechanical stirrer, distillation condenser and a thermometer, was charged with 160 g of mineral spirits, 83 g of 2-ethyl hexanoic acid, 70 g of a glycol ester of a fatty acid, 70 g of methyl carbitol and 331 g of barium hydroxide monohydrate. The reactor contents were then heated slowly to 140°C, and water was removed. Carbon dioxide was then turned on at a rate of 1 LPM (liter per minute) for 1 to 1.5 hours, and water of the reaction was removed. The product was filtered using a filter aid at 140°C and a very light colored liquid product containing 36% barium was obtained.

Example 5

A one-liter resin kettle, equipped with a mechanical stirrer, distillation condenser and a thermometer, was charged with 160 g of mineral spirits, 83 g of 2-ethyl hexanoic acid, 70 g of propylene glycol butyl ether, 70 g of methyl carbitol and 331 g of barium hydroxide

monohydrate. The reactor contents were then heated slowly to 140°C, and water was removed. Carbon dioxide was then turned on at a rate of 1 LPM (liter per minute) for 1 to 1.5 hours, and water of the reaction was removed. The product was filtered using a filter aid at 140°C and a very light colored liquid product containing 37% barium was obtained.

Example 6

A one-liter resin kettle, equipped with a mechanical stirrer, distillation condenser and a thermometer, was charged with 160 g of mineral spirits, 83 g of 2-ethyl hexanoic acid, 70 g of dipropylene glycol methyl ether, 70 g of methyl carbitol and 331 g of barium hydroxide monohydrate. The reactor contents were then heated slowly to 140°C, and water was removed. Carbon dioxide was then turned on at a rate of 1 LPM (liter per minute) for 1 to 1.5 hours, and water of the reaction was removed. The product was filtered using a filter aid at 140°C and a very light colored liquid product containing 34% barium was obtained.

Example 7

A one-liter resin kettle, equipped with a mechanical stirrer, distillation condenser and a thermometer, was charged with 160 g of mineral spirits, 83 g of 2-ethyl hexanoic acid, 70 g of triethylene glycol, 70 g of methyl carbitol and 331 g of barium hydroxide monohydrate. The reactor contents were then heated slowly to 140°C, and water was removed. Carbon dioxide was then turned on at a rate

of 1 LPM (liter per minute) for 1 to 1.5 hours, and water of the reaction was removed. The product was filtered using a filter aid at 140°C and a very light colored liquid product containing 31% barium was obtained.

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Example 8

The performance of the highly over-based (alkyl) phenol-free barium complex described in Example 1 was compared against an alkyl phenol-containing 34% barium, stabilizer composition containing 9% barium, 2% Zn (zinc octoate), 3.5% P (diphenyl isodecyl phosphite), 4% carboxylic acid, 0.5% anti-oxidant, 2% beta-diketone (dibenzoyl methane) and diluent.

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The performance of these stabilizers was evaluated in a PVC formulation containing 100 parts of PVC resin, 45 parts phthalate plasticizer, 2.5 parts of epoxidized soybean oil and 2.5 parts of a stabilizer.

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The stabilized PVC compounds were then milled at 350-360°F for five minutes at 25-mil thickness. The thermal stability was carried out at 380°F over seventy minutes. Stabilizer containing new phenol-free barium demonstrated better early to mid-term performance in color as measured by a calorimeter as an indication of yellowing (see Table 1) than a stabilizer containing alkyl phenol derived barium. However, at seventy minutes both stabilized PVC compounds turned black.

25

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Table 1

Time (min.)	Stabilizer with Phenol- Free Barium (b-values)	Stabilizer Containing Alkyl Phenol-Derived Barium (b-values)
0	-1.92	2.06
10	-1.37	0.5
20	-1.39	-0.54
30	-0.18	0.74
40	2.8	4.35
50	4.9	4.89
60	13.79	13.48